HIGH TEMPERATURE PROTECTIVE COATINGS FOR REFRACTORY METALS

PROGRESS REPORT NO. 2

PREPARED UNDER CONTRACT NO. NASw-1030

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

UNION CARBIDE CORPORATION
CARBON PRODUCTS DIVISION
PARMA, OHIO

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I. INTRODUCTION

The need for improved protective coatings for the refractory metals (Mo, Cb, Ta, and W) remains critical for many high temperature applications, since the life provided by available coatings is too brief to take full advantage of the strength and temperature capabilities of these metals.

Because of their high temperature strength, molybdenum, columbium, tantalum, and tungsten have been considered for leading edges, attachments, and structural members for re-entry spacecraft. Since, during re-entry, leading edges encounter temperatures in the range 3000° to 3500°F under oxidizing conditions, a protective coating is needed to prevent corrosion. However, protective coatings for the refractory metals appear at present to be limited to ~2600°F for extended service.[1,2]

Under Contract NASw-1030 (initiated October 23, 1964), we are investigating iridium as a protective coating for columbium and tantalum. Prior work[3] involving iridium as a protective coating for graphite has demonstrated that this metal is impervious to oxygen and sufficiently resistant to oxidation to function adequately as a barrier to corrosion in air at high temperatures. The questions to be answered by this research are concerned with interdiffusion, chemical compatibility, and mechanical behavior of iridium in contact with tantalum and columbium.

During the period 23 January 1965 to April 1965, research was concerned with (1) methods of applying iridium to the refractory metal substrate, (2) the chemical and mechanical behavior of the coating-substrate system, and (3) qualitative oxidation tests.

II. SUMMARY

A. Research Results

The rate of interdiffusion of iridium and tantalum is being determined at 1500°C. The rate of increase of the diffusion zone appears to follow a parabolic rate expression; however, additional annealing experiments are being carried out to explain more fully the growth mechanism. Diffusion experiments were also carried out at 1200°, 1300°, and 1400°C with diffusion annealing times ranging from one to four hours. The results derived from these experiments are being evaluated and will appear in the next Progress Report.

Microbend tests were used to demonstrate the ductility of hot-rolled iridium and iridium on tantalum. As-rolled specimens were bent at an angle greater than 90 degrees without fracture. Annealing of roll-bonded iridium-tantalum couples at 1500°C resulted in the formation of a diffusion zone which cracked under slight loads in the bend tests; however, the iridium coat cracked only when the bend angle exceeded 21 degrees.

An initial study of tungsten as a diffusion barrier between iridium and columbium showed a reaction zone only at the Ir-W interface. The total diffusion zone thickness was the same as that produced in the absence of a barrier layer.

Iridium has been electrodeposited on tantalum and columbium substrates. In conjunction with this phase of the program, substrate surface preparations and voltage-current characteristics of the electrolytic cell have been determined for preparing suitable oxidation test specimens of iridium on tantalum and columbium.

The mechanical behavior of electrodeposited iridium was found to differ from that of rolled iridium. The former was found to be brittle when deposited on tantalum and columbium, but ductile when deposited on copper. Iridium roll-bonded to tantalum and columbium is very ductile. The reason for such mechanical behavior is not fully explained by this investigation. Further work on the mechanical behavior, beyond the scope of this program, is suggested.

Three tantalum rods electroplated with a 2- to 3-mil coating of iridium failed in two minutes upon oxidation in an oxy-methane flame at 1450° C. Cause of failure in these preliminary tests was attributed to pinholes in the iridium coatings.

III. RESEARCH PROGRAM

During this report period, the original work statement for Contract NASw-1030 was amended, and the termination date has been extended to October 1965. The contract now includes research on the iridium-molybdenum and the iridium-tungsten systems.

This program, involving a study of the application of iridium coatings to the refractory metals (Ta, Cb, W, and Mo) and their suitability as protection against oxidation at elevated temperatures, is concerned with four main areas of research. As shown diagrammatically in Figure 1, these areas consist of (1) sample preparation, (2) chemical compatibility studies, (3) mechanical compatibility studies, and (4) oxidation studies.

A. Sample Preparation

Iridium deposition from a fused salt is the most promising of the coating techniques which are amenable to coating large, intricate geometrical shapes and, therefore, has been selected as one of the main methods of sample preparation. This method will not only provide specimens for further study, but it will also allow an assessment of the influence of process variables on purity, hardness, and bonding of the coating to the substrate.

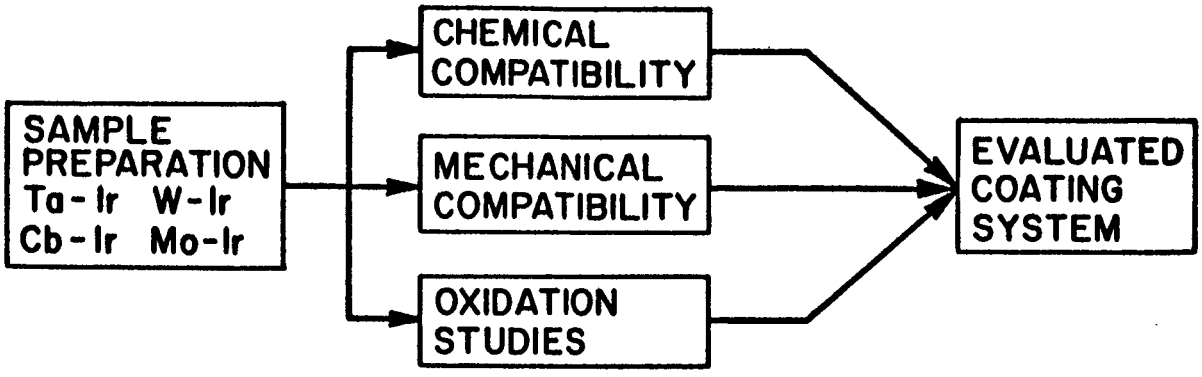


Figure 1. Research Program — Oxidation Protective Coatings for Refractory Metals.

N-7308

In addition to electroplating, roll bonding and pressure bonding provide other means of obtaining these specimens. Since roll bonding often results in preferred crystallite orientation, the method of composite fabrication may alter the physical and chemical characteristics of the coating-substrate system. In addition, the latter methods are particularly amenable to the fabrication of coated sheets. Since many test specimens will be required for our future (MAB) coating evaluation procedures, we will use all three methods of sample preparation.

B. Chemical Compatibility

The character of the interface between coating and substrate is being established by optical and X-ray metallography. This work will establish the extent of interdiffusion and intermetallic phase formation as a function of time and temperature. Although unalloyed iridium is impermeable to oxygen, the behavior of intermetallic phases and the influence of interdiffusion on the oxidation resistance of iridium must be studied.

C. Mechanical Compatibility

The strength of the coating substrate bond will be determined by conducting room temperature tensile and elongation tests in general accordance with Sections 3 and 7 of the Materials Advisory Board Report MAB-201-M

entitled "Procedures for Evaluating Coated Refractory Metal Sheet." Metallographic studies will be performed on the base metal and the coating system to determine the per cent of recrystallization in the base metal resulting from the coating process and to determine other interactions between the coating and substrate as specified in Section 4 of the MAB-201-M. In addition, coated-tensile-type specimens will be subjected to varying degrees of elastic and plastic prestrain at various temperatures and subsequently oxidized. Retention of oxidation protection for a prescribed period of oxidation exposure will be the criterion for the coating strain tolerance (see Section 9, MAB-201-M).

D. Oxidation Studies

For the oxidation studies, both furnace and oxyacetylene flame heating will be used in general accordance with Materials Advisory Board specifications outlined in report MAB-201-M.

IV. EXPERIMENTAL

A. Materials

The iridium used in this program was high-purity sheet approximately 2 inches wide by 6 inches long purchased from Engelhard Industries, Inc. Sheet thicknesses of 0.005, 0.020, and 0.040 inch were used, depending upon the specific application. The 0.020- and 0.040-inch-thick sheet iridium was cut to the desired size using a water-cooled diamond cut off wheel; the 0.005-inch-thick sheet was sheared to size after annealing with an open flame. The tantalum and columbium ($^1/_4$ inch diameter rods and the 0.020-inch-thick sheet) were purchased from the Stellite Division of Union Carbide Corporation. These metals were cut to the desired size and shape using normal machining practices. The iridium and potassium cyanides were high-purity analytical reagent grades.

B. Sample Preparation

The experimental apparatus and procedures used for obtaining coating-substrate composites by fused salt electrodeposition, roll bonding, and pressure bonding were described in the previous Progress Report. The Experimental section of this report will describe experimental modifications and procedures developed during this period.

1. Fused Salt Electrodeposition of Iridium

Basically, the same type of fused salt cell is being used to electroplate iridium as described in the previous report. The modifications made in the basic equipment involved the construction and use of a constant voltage direct current power supply; in addition, for a large part of this period, the alundum argon inlet tube was submerged in the molten bath. Bubbling of argon into the molten bath did not produce the desired results and was discontinued. The electroplating procedure was modified slightly: alternating current is no longer used to charge the molten bath with iridium; instead, pieces of a solidified bath that was producing the desired results are added to a new salt bath. This procedure eliminated the time-consuming induction period necessary to put iridium into solution in the molten bath. Also, all electrodeposits are now started with a strike at 100 amp/feet^2 for about ten minutes. The current density is then lowered to the desired level.

A standardized procedure for preparing the substrate-metal surface prior to electrodeposition is being sought which will consistently yield a metallurgically bonded coating-substrate composite. To achieve this objective, substrate metals were subjected to a variety of surface preconditioning treatments, including vacuum degassing at elevated temperatures, mechanical abrasion, chemical cleaning and activation of surface sites, and iridium slurry coating and sintering prior to electrodeposition.

2. Roll Bonding

Roll bonding may provide a rapid and efficient means of obtaining specimens for oxidation and mechanical tests. This technique of preparing samples was described in Progress Report No. 1. A 25 per cent volume reduction

in the Ta-Ir composite was found to be adequate for obtaining a good metal-to-metal bond. The roll-bonding process will be used as an alternate method of preparing future test specimens.

3. Pressure Bonding

A single-pressure bonding experiment performed at the start of this investigation resulted in a good adherence between the tantalum and iridium and in a poor adherence between the columbium and iridium. Cylindrical specimens of Ta, Ir, and Cb measuring $^{3}/_{16}$ inch diameter were placed in a molybdenum holder and annealed. The one-inch diameter heater in the vacuum annealing furnace limited the holder and sample size. The holder and plug used in this experiment, machined from pure molybdenum rather than from a Mo-0.5 titanium alloy used by Passmore[3] resulted in embrittlement and complete destruction. The difficulties encountered in the first experiment regarding size and holder material will be resolved by the proposed hot-pressing techniques.

Plans are being made to prepare specimens for oxidation and bend tests by pressure bonding techniques. A vacuum hot press, capable of using a $2\ ^{1}/_{2}$ inch die, is now available and will be employed to pursue this technique of sample preparation. The die and plunger will be made of high-strength graphite.

4. Electrodeposition of Refractory Metals

The possibilities of using multiple layered composites between the iridium and the refractory metals are being examined. Experimental specimens are being prepared by electrodeposition of tungsten and columbium on an iridium substrate. The fused-salt technique for electroplating refractory metals, developed at the Parma Technical Center (Union Carbide Corporation, Carbon Products Division) by G. W. Mellors and S. Senderoff, consistently produces dense, coherent deposits by the electrolysis of the molten fluoride.

C. Sample Evaluation Techniques

1. Diffusion Studies

Specimens prepared by electroplating iridium on the substrate metal, or the reverse process, were used to determine the total reaction zone thickness. Most specimens were heated under vacuum to the desired temperature, held at temperature for a predetermined length of time, and then furnace-cooled to room temperature. Some specimens were preheated to establish a good chemical bond prior to annealing.

Normally, thirty minutes are required to attain a temperature of 1200°C. In order to determine the thickness of diffusion zone resulting from heating and cooling the sample, a specimen was heated and held at 1200°C for thirty minutes. The diffusion zone in this case was less than one micron thick. Since only a few minutes were required in going from 1200° to 1500°C, the heating and cooling periods were considered to have a neglibible effect on annealing times at 1500°C. After all specimens were subjected to the desired heat treatment, they were metallographically polished on an edge showing the coating, the substrate, and the reaction zone. The thickness of the reaction zone was then determined from photomicrographs and by direct measurement using a Tukon Hardness Tester with a calibrated eyepiece. Because of irregularities in the reaction zone boundary, all measurements of the thickness represent an average value of several determinations. A single measurement by either method was reproducible to within ± 0.4 microns.

2. Mechanical Compatibility

a. Microbend Tests

The microbend test apparatus used to observe the microstructure of a specimen during the application of a bending stress was described in the previous Progress Report.

b. Standard Bend Testing

A stainless-steel bend fixture was constructed according to the specifications set up by the Materials Advisory Board. The fixture, shown in Figure 2, will allow a 2-inch x 0.5-inch x 0.020-inch specimen to be bent

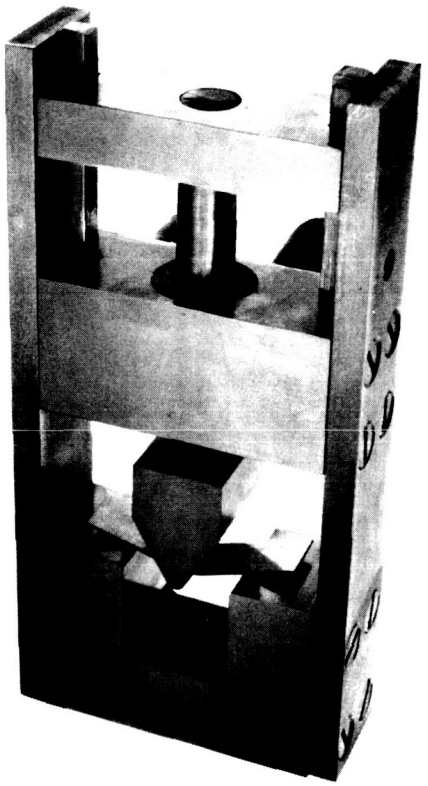


Figure 2. Standard Bend Fixture N-7035

as a single beam in three-point loading. The male die, made of hardened steel, has a radius of 0.080 inch (corresponding to a 4t bend).

3. Oxidation Tests

Preliminary oxidation tests on iridium-coated tantalum were conducted in an oxy-methane flame in air at one atmosphere pressure. The gas flow rate was maintained at 11 CFH of oxygen and 5 CFH of methane (natural gas).

Specimen temperatures were adjusted by varying the distance between the torch flame and the specimen, a distance which ranged from 0.5 inch to 5 inches. Surface temperatures were measured with a micro-optical pyrometer that could be read to ±2°C. Surface temperature correction was

made using an emissivity of 0.50, which is the value found during the oxidation of iridium[4] in air at 1600°C. An error of ±0.1 in the assumed emissivity corresponds to an error of approximately ±25°C at 1000°C and of ±50°C at 2000°C.

The test specimens, 1/4 inch diameter x 3 inches tantalum rods coated with a 2 to 5 mil thickness of iridium by electrodeposition, were mounted in a one-inch diameter graphite base. The base, with the test specimen in an upright position, was submerged in water such that only 2 inches of the iridium-coated tantalum extended above the water level.

Since the oxidation tests were of a preliminary nature to check the testing method, these experiments were of five-to ten-minute duration.

4. Visual Examination

All coating-substrate composites, regardless of the method of preparation, were examined for external flaws with the unaided eye and with a low-powered microscope. Specimens that could be sectioned, such as those used for studying diffusion effects, were metallographically polished and microscopically examined.

V. RESULTS AND DISCUSSION OF RESULTS

A. Diffusion Studies

1. The Ta-Ir System

Iridium-coated tantalum specimens prepared by electrodeposition were studied by metallographic techniques after annealing at various times and temperatures. A coated specimen measuring ~3/4 inch x 1 inch x 0.024 inch was preheated for five minutes at 1680°C to insure that good adherence was obtained prior to the diffusion studies. The short time annealing produced a diffusion bond between the iridium coating and the tantalum substrate and a total reaction zone measuring ~5.5 microns. Figure 3 shows that this

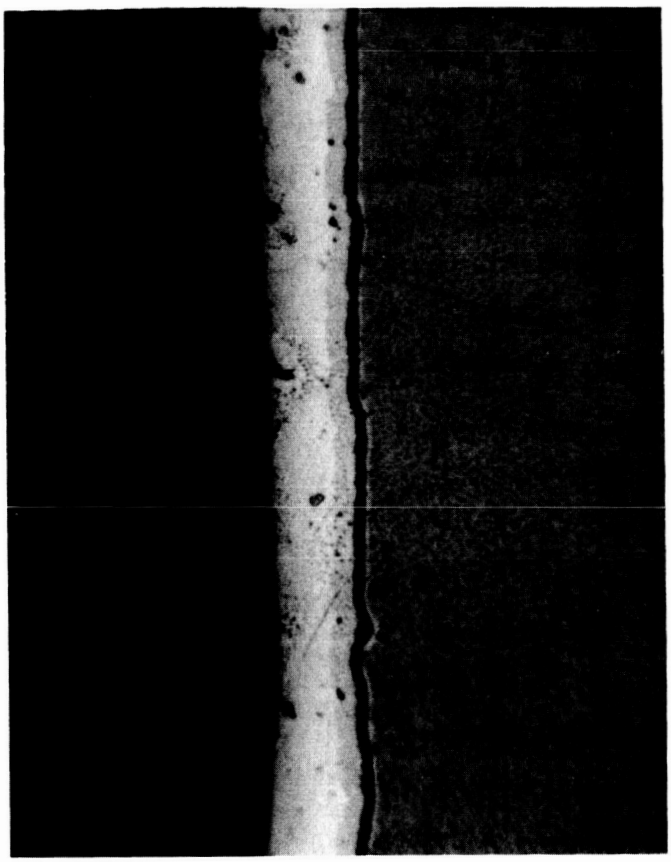


Figure 3. Electrodeposited Ir-Ta Specimen Annealed Five Minutes at 1680°C, 750 X Mag. N-7044

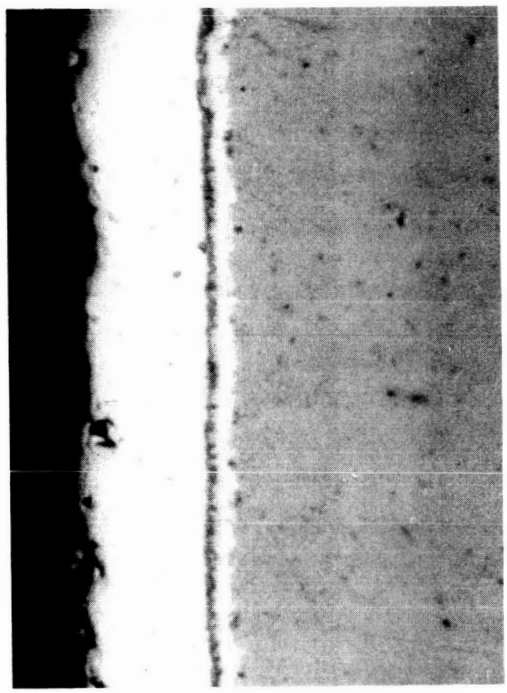
diffusion zone consisted of three distinct regions. Although no positive identification has been made of the phases observed in the reaction zone, the equilibrium phase diagram[5] for the tantalum-iridium system shows that there are four intermediate phases. On the basis of the constitution diagram, the reaction zone phase adjacent to the tantalum would be expected to be the τ phase and that adjacent to the iridium, $TaIr_3$. The selective etching necessary to reveal the intermediate phases α_1 and α_2 would destroy the tantalum substrate to the extent that no accurate measurements of the total reaction zone would be possible.

The preheated specimens discussed above were sectioned into three pieces and annealed at 1500°C for one, two, and three hours to study the effect of time on the reaction zone thickness. The photomicrographs shown in Figure 4 illustrate the change in reaction zone thickness resulting from the three annealing times. In these experiments, the original reaction zone thickness (d_o) minus the reaction zone thickness after annealing (d_f) indicates that (1) additional annealing experiments will be required to determine the rate-controlling mechanism at 1500°C and (2) the preheat time and temperature (prior to annealing) should be minimized to reduce the initial reaction zone (d_o).

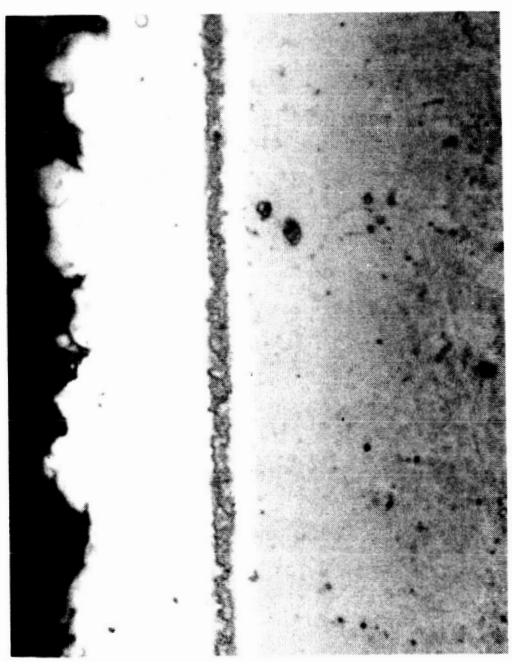
Annealing experiments were also carried out at 1200°C to determine the time at temperature necessary to obtain a good bond with the minimum amount of reaction zone. This temperature corresponds with that used in the roll bonding experiments and was selected in an attempt to duplicate the ductility and trace amounts of diffusion zone observed in the roll bonded specimens. Annealing times of four hours and one-half hour were chosen to correspond to the time at temperature required for the rolling operation. Figure 5a is a photomicrograph of an iridium-tantalum specimen annealed one-half hour at 1200°C, disclosing the initial formation of an intermediate phase in the iridium coating. This minute amount of phase region did not form a continuous boundary between the tantalum and iridium; however, an excellent bond was obtained between the coating and substrate. Most of the small islands of intermediate phase measured less than one micron in thickness.

As can be seen in Figure 5b, annealing specimens for four hours at 1200°C modified the thickness and produced a 4.0-micron thick continuous intermediate phase boundary between the tantalum and iridium. Trace amounts of another phase region appeared as a dark line adjacent to the tantalum substrate.

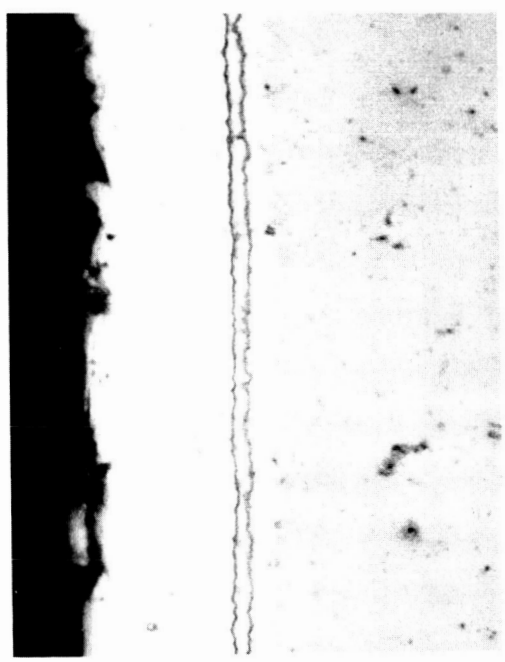
The rate of formation of the total reaction zone between iridium and tantalum is being investigated at 1200°, 1300°, and 1400°C. Diffusion annealings of one, two, three, and four hours at these temperatures have been carried out; the specimens are being presently examined. This information may provide a total reaction zone rate temperature dependence.



4a. Annealed One Hour
N-7045

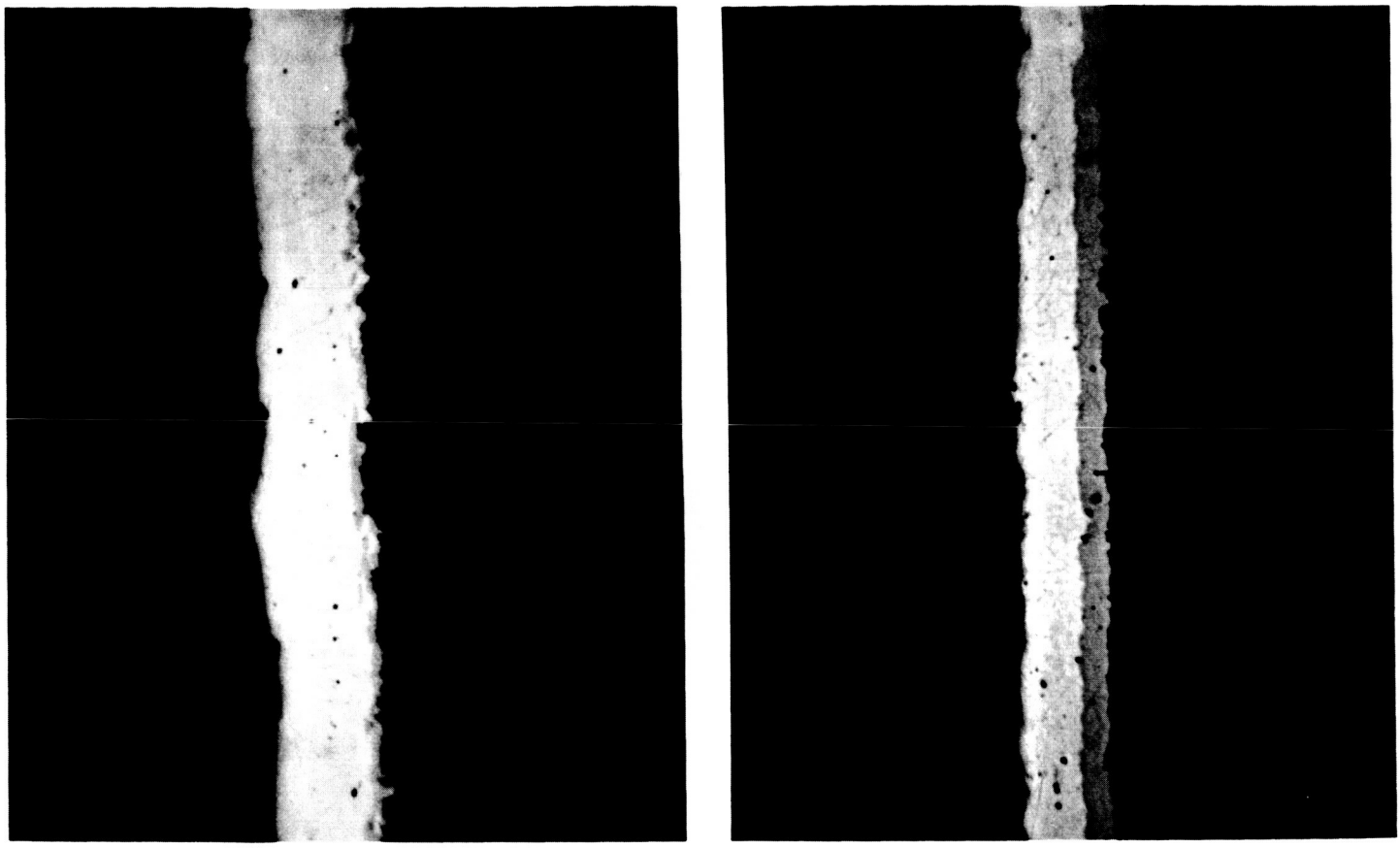


4b. Annealed Two Hours
N-7046



4c. Annealed Three Hours
N-7047

Figure 4. Electrodeposited Ir-Ta Specimens Reannealed at 1500°C.



5a. One-Half Hour, 750X Mag.
N-7049
Neg. No. 1444

5b. Four Hours, 750X Mag.
N-7050
Neg. No. 1445

Figure 5. Electrodeposited Ir-Ta Specimens Annealed at 1200°C

2. The Cb-Ir System

No additional information has been obtained on diffusion in the columbium-iridium system since the previous Progress Report.

B. Mechanical Compatibility by Microbend Tests

1. The Ta-Ir System

A Ta-Ir specimen that was reduced 20 per cent by hot rolling was sectioned to provide two specimens for microbend tests. One specimen was

tested in the as-rolled condition, and the other was vacuum annealed for four hours at 1500°C before testing. Annealing produced a diffusion zone of 15 microns and recrystallized the elongated iridium grains produced by rolling. The specimen in the as-rolled condition was bent to an angle greater than 90 degrees, and no cracks were observed in the coating or the substrate. The annealed specimen developed cracks in the diffusion zone when very small loads were applied. In spite of the diffusion zone cracks, bending was continued to an angle of approximately 21 degrees before the iridium coating began to crack along the grain boundaries.

The excellent ductility displayed by roll-bonded iridium makes this method of applying iridium promising for obtaining coated sheets. If subsequent attempts at roll bonding continue to produce ductile composites, it may be possible that iridium-clad sheets of refractory metals can be subjected to room-temperature forming operations.

2. The Cb-Ir System

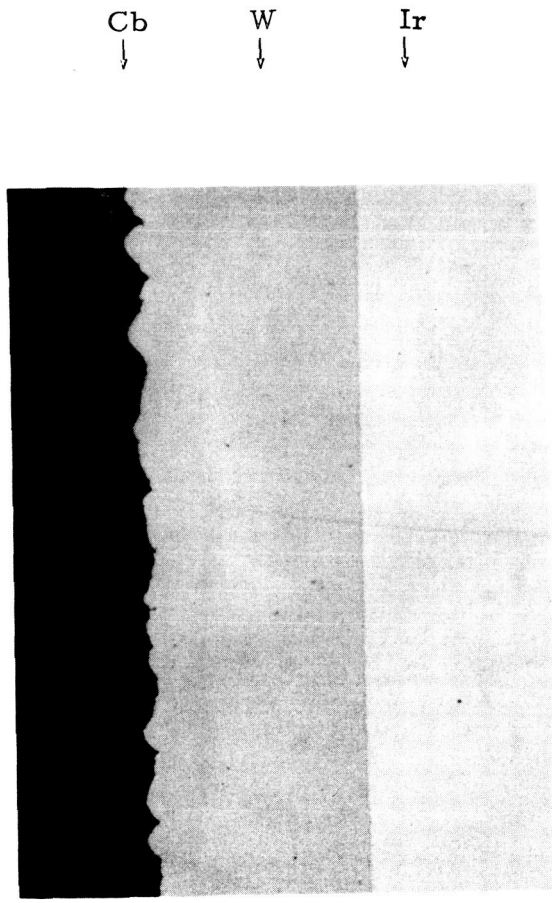
The first attempt at roll bonding columbium to iridium failed. Nevertheless, the piece of iridium that did not adhere to the columbium was metallographically polished and tested using the microbend tester. The iridium was bent to an angle of greater than 90 degrees, and no cracks were observed.

C. Diffusion Barriers

The benefit derived from a diffusion barrier placed between the iridium coating and substrate is being considered. Passmore[3] of ManLabs, Inc. selected promising diffusion barriers for refractory metals. From nine potential barriers evaluated for interdiffusion with tantalum, he selected tungsten, rhenium, and ruthenium. Of the eight evaluated with Cb, he selected tungsten, osmium, and zirconium. On the basis of Passmore's findings, we selected tungsten as a possible barrier because it shows promise for both Cb and Ta and because it can be readily deposited by electrodeposition.

To investigate the use of tungsten metal as a barrier material between Cb and Ir, three specimens were prepared by fused salt electrodeposition. Coatings of tungsten and columbium were applied to 10-mil iridium sheet which was used as the substrate material.

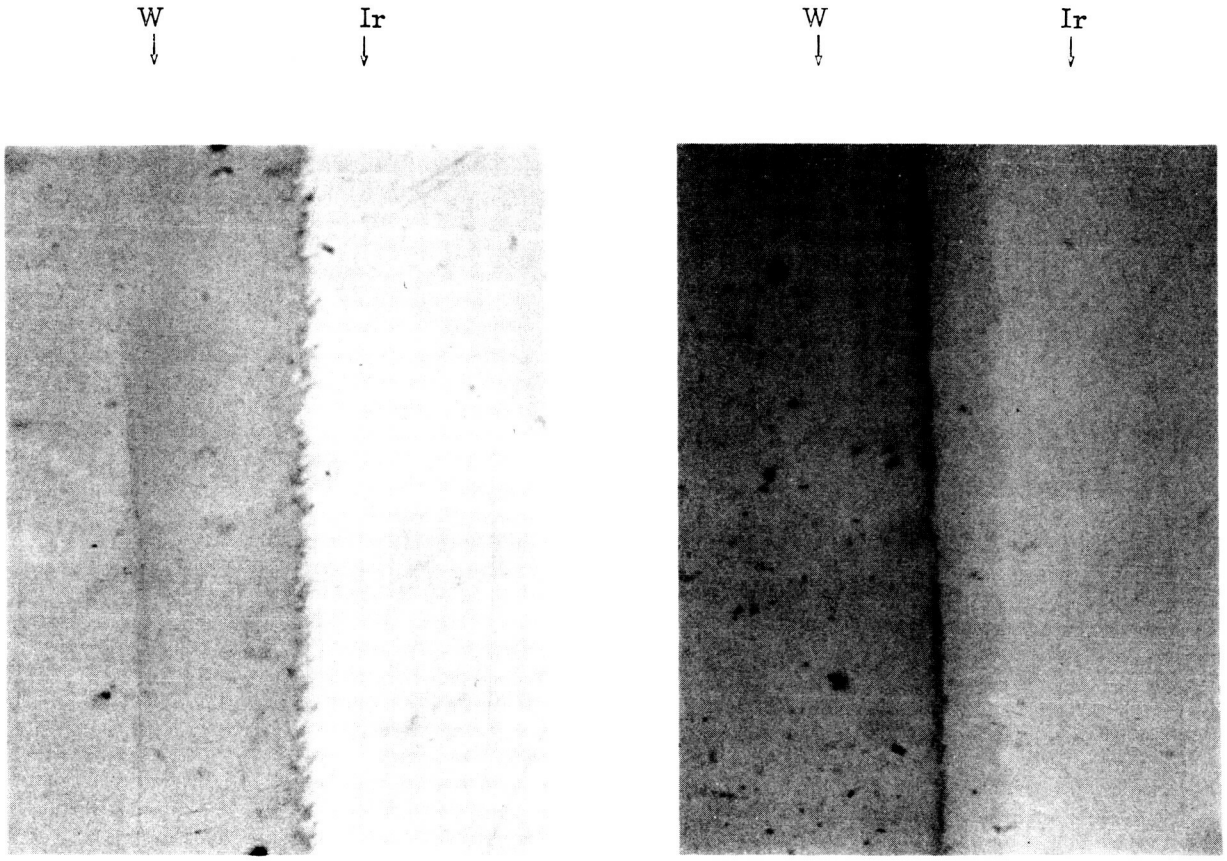
Figure 6 represents the Cb-W-Ir specimens photographed in the as-deposited conditions. Good adherence was obtained between each layer.



N-7105

Figure 6. Double Layer Coating of Cb and Ta on Iridium by Fused Salts. Cb-W-Ir Interfaces at 100X Mag.

The W-Ir interface is shown (Figure 7) to illustrate the effect of annealing. The Cb-W-Ir specimen was annealed for four hours at 1350°C, resulting in a diffusion zone at the W-Ir interface measuring approximately 6 microns (see Figure 7b). This diffusion zone thickness is 2 microns less than that previously observed in the Cb-Ir specimen. Based on this result, it appeared that a tungsten barrier between Cb and Ir would not reduce the compound formation enough to justify its use.



7a. As-deposited Condition 1065 X Mag. N-7106

7b. After Annealing Four Hours at 1350°C at 1065 X Mag. N-7107

Figure 7. Electrodeposited W on an Ir Substrate.

D. Fused Salt Electrodeposition

Electrodeposition provides a means of rapidly coating intricate geometrical shapes of refractory metals with iridium. Two important factors involved in obtaining a smooth, adherent, pore-free coating are (1) substrate surface preparation prior to electrodeposition and (2) the voltage current characteristics of the particular system being used for the electroplating process.

1. Substrate Preparation Prior to Electrodeposition

Improper surface preparation prior to electroplating invariably results in an irregular coating which is often nonadherent.

In this investigation, copper substrates were degreased by washing them in acetone, cleaned by mechanical abrasion or dilute nitric acid, and finally treated again with acetone. The tantalum and columbium surfaces were also degreased with acetone and then subjected to one or more of the following cleaning processes: (1) vacuum degassing, (2) mechanical abrasion, (3) applying a prior subcoat of iridium by the slurry dip and sinter technique, and (4) various chemical cleaning methods (e. g., acid dip, base dip, or anodic and cathodic etching). In addition, some of these substrates were subjected to the elaborate surface treatments recommended by the Defense Materials Information Center (DMIC Memorandum 35, October 9, 1959) "Procedures for Electroplating Coatings on Refractory Metals." Iridium electrodeposited on tantalum and columbium was frequently nonadherent.

In the case of tantalum and columbium substrates, surface preparation alone was not adequate for consistently obtaining well-adherent coatings.

Interactions of the refractory metals with impurities in the fused salt electrolyte may also cause nonadherence of the electrodeposited coatings. Typical of those specimens on which the iridium did not adhere was the presence of an extremely dark layer between the coating and substrate. This dark barrier layer which prevented the iridium from being metallurgically bonded to tantalum or columbium very likely formed as a result of chemical reaction between the substrate metals and chemical species present in the molten salt. X-ray diffraction and X-ray fluorescence methods of analysis were

used to examine the dark barrier layer that formed on tantalum. Because of the small amounts present, no positive identification of this material could be made.

Several precautions were taken to prevent the contamination of the substrate by the fused salt bath. These precautions were : (1) purging the bath with dry, high-purity argon to assure the removal of water which is a commonly known contaminant in fused salt baths even at high temperatures; (2) pre-electrolyzing, using copper or high-purity graphite as cathodes to remove cation impurities; and (3) precoating the substrate metal with iridium by slurry coating and sintering to provide a surface which would be inert to attack by contaminants in the fused salt bath.

Although these precautions and prior surface treatment of the substrate did in many instances improve the coating, they did not consistently produce adherent coatings.

2. Voltage-Current Characteristics of the Fused Salt Cell

A constant voltage, direct current power source, was used to obtain the voltage-current characteristic curve for the fused salt plating bath. Although the method used for determining the current was not very precise (a standard cell is normally used instead of an ammeter), the results give an approximate indication of the cell potential limits within which the desired results would be expected to occur. The results, which are only applicable to our specific plating operation, are shown in Figure 8 and 9 for the electrodeposition of iridium on copper and tantalum, respectively. The results indicate that the cell potential range needed to produce an iridium coating that increased in thickness with time was between about 0.4 and 1.5 volts. Above 1.5 volts, an increase in the current may be due to the motion of charged species other than the iridium complex; in addition, the cell potential may be sufficient to decompose the electrolyte. Within 0.4 and 1.5 volts, the higher the cell potential, the greater the current density and, therefore, the deposition rate. The nature of the deposit (such as the formation of dendrites or a porous coating) may vary considerably with deposition rate; and, as reported by Withers and Ritt, [6] the cathode efficiency is strongly dependent upon current density.

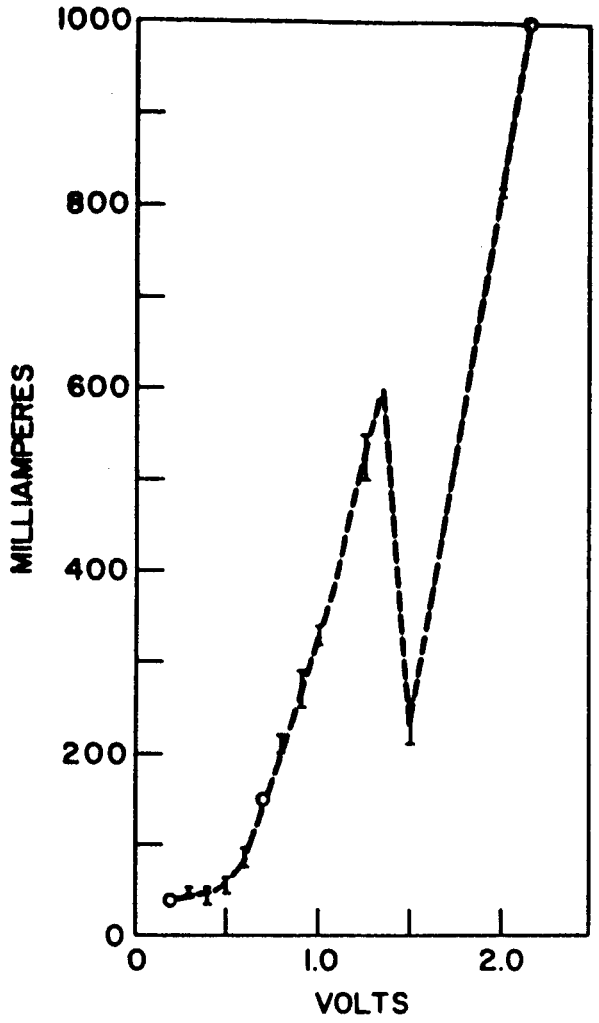


Figure 8. Voltage-Current Characteristic, Copper Substrate.

N-7096

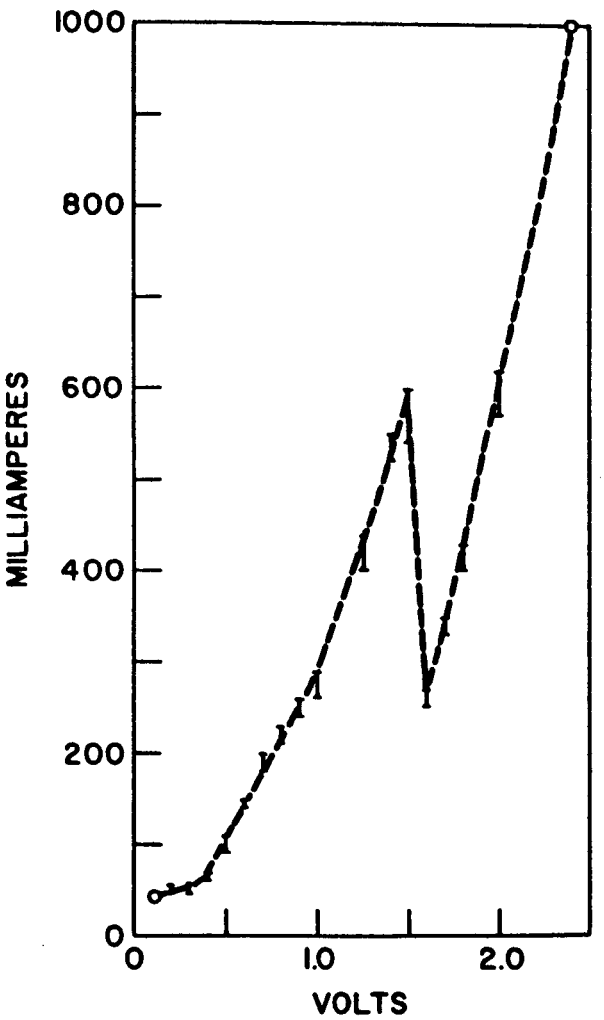


Figure 9. Voltage-Current Characteristic Curve, Tantalum Substrate.

N-7095

E. Mechanical Behavior of Iridium

Iridium exhibits a high degree of work hardening, a behavior which is unusual for a metal having a face-centered cubic structure. The latest study on the deformation characteristics of iridium by Hieber, Mordike, and Haasen[7] suggests that very small amounts of impurities segregated at the grain boundaries are the cause of the unusual work hardening behavior. Unfortunately, the impurities causing the embrittlement are not known and seem to be very much lower than those usually required to produce grain boundary weakness. In a similar investigation of the deformation characteristics of rhodium, Calverley and Rhys[8] also concluded that grain boundary segregation of unknown impurities was the cause of embrittlement.

The unusual brittle behavior of iridium was also observed during this investigation. However, of greater significance was the observation that many of the iridium coatings that were electrodeposited on copper were as ductile as would be expected of face-centered cubic metals. Quite often, an iridium-coated copper sheet could be folded repeatedly by hand along the same line without the formation of cracks. Iridium electrodeposited on tantalum and columbium, however, was not ductile. Microbend tests of these latter composites produced cracks at a bend angle of less than 10 degrees, the cracks propagating along the grain boundaries. On the other hand, iridium roll-bonded with tantalum or columbium was bent to an angle greater than 90 degrees with no observable cracks forming.

Since sheet iridium is fabricated in a manner similar to that used for roll bonding (exclusive of the canning operation needed to protect the substrate metals from oxidizing), a 0.020-inch-thick piece of as-received iridium was examined in the microbend tester. The result is shown in Figure 10, a photomicrograph taken at a magnification of 250X. At a bend of less than 10 degrees, cracks developed propagating along the grain boundaries. Two strips of iridium, cut from the same sheet as the above sample, were heated to 1400°C under vacuum for ten minutes. While still under vacuum, one of these strips was slowly cooled to room temperature and the other was quenched into a silicon oil bath. Both samples were bent to 33 degrees before microscopic examination revealed cracks; subsequently, they were bent through greater than 90 degrees without complete destruction..

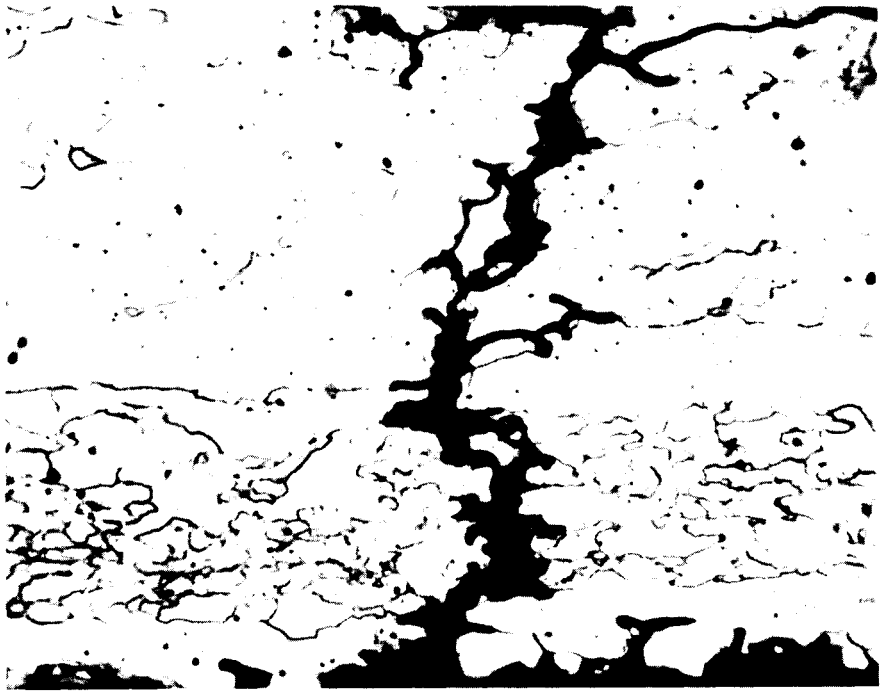


Figure 11. Photomicrograph of an Iridium Strip Bent to less than 10 Degrees. 250 X Mag.

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Although the above experiments are not sufficient for a detailed analysis of the mechanical behavior characteristic of iridium, they nevertheless substantiate the grain boundary weakness discovered by other investigators.[7,8] Iridium can be plastically deformed at elevated temperatures. Cracks that appear upon deformation at room temperature and propagate along grain boundaries are usually indicative of an impurity that is soluble in the metal at elevated temperature but precipitates out and agglomerates at the grain boundaries upon cooling to room temperature. The meager evidence accumulated in this and other investigations emphasizes the need for a research program designed to determine the effect of specific impurities on the deformation characteristics of iridium. A clear understanding of the deformation characteristics of iridium would be of interest both from the practical and theoretical standpoint.

F. X-ray Diffraction and Fluorescence Analysis

A comparison was made between roll-bonded and electroplated iridium by means of X-ray diffraction and X-ray fluorescence analyses. The X-ray diffraction patterns of iridium electroplated on tantalum showed a random orientation of the crystallites, whereas the X-ray diffraction patterns of iridium roll bonded to tantalum showed preferred orientation. X-ray diffraction patterns and X-ray fluorescent patterns of the roll-bonded specimens showed the presence of aluminum. Although the preferred orientation of the iridium was expected, the presence of aluminum metal was not. In the roll-bonding operation, aluminum oxide powder was used as a barrier to prevent bonding between the specimen and the metal can. Apparently, the aluminum oxide was reduced to aluminum, which may have diffused into the iridium.

1. Oxidation Tests

The rate at which iridium oxidizes and the permeability of iridium to oxygen have been adequately investigated at high temperatures.[9] However, at elevated temperatures, interdiffusion and reaction between the coating and substrate will occur and may (1) reduce the effective coating thickness, (2) alter the oxidation rate and permeability of the coating, and (3) embrittle the coating and/or substrate metal. In addition, the method of fabrication may produce a coating containing pinholes or microcracks not readily detectable. Oxidation tests must be performed on the iridium-coated refractory metals if iridium is to be thoroughly evaluated as a coating material.

In preliminary oxidation tests, three $\frac{1}{4}$-inch diameter tantalum rods that were electroplated with a 2- to 3-mil-thick coat of iridium were oxidized using an oxygen-methane torch. When exposed to the flame in air, the tantalum substrate started oxidizing after ten minutes at 1450°C. According to oxidation experiments[9] performed with simulated air (20 per cent oxygen and 80 per cent argon at one atmosphere total pressure) impinging normal to a pure iridium surface at 12,000 feet per minute, the oxidation rate at 1450°C is about 0.06 mil per minute. An iridium coating 2 to 3 mils thick should

have lasted between thirty and fifty minutes. Premature failure of the test specimens may have been caused by the presence of pinholes or microcracks in the iridium. The specimens are presently being investigated using metallographic techniques.

VI. FUTURE PLANS

The preparation of specimens for oxidation tests will be emphasized during the next report period. Tantalum, columbium, molybdenum, and tungsten will be coated with 0.003 inch to 0.005 inch of iridium by electrodeposition, roll bonding, or pressure bonding. An electrolytic cell has been designed and constructed for carrying out electrodeposition simultaneously on several pieces of refractory metal. The roll bonding and pressure bonding will be carried out so as to completely encapsulate the refractory metal substrate.

The iridium-coated metals will be subjected to both oxy-methane flame and air furnace oxidation tests.

The annealed iridium-tantalum specimens will be examined to determine the rate of reaction as a function of time and temperature. In addition, these studies will be extended to include Ir-Cb, Ir-Mo, and Ir-W systems.

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July 10, 1965

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